



Metal fractionation in marine sediments acidified by enrichment of CO₂: A risk assessment



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ABSTRACT

Carbon-capture and storage is considered to be a potential mitigation option for climate change. However, accidental leaks of CO₂ can occur, resulting in changes in ocean chemistry such as acidification and metal mobilization. Laboratory experiments were performed to provide data on the effects of CO₂-related acidification on the chemical fractionation of metal(lloid)s in marine-contaminated sediments using sequential extraction procedures. The results showed that sediments from Huelva estuary registered concentrations of arsenic, copper, lead, and zinc that surpass the probable biological effect level established by international protocols. Zinc had the greatest proportion in the most mobile fraction of the sediment. Metals in this fraction represent an environmental risk because they are weakly bound to sediment, and therefore more likely to migrate to the water column. Indeed, the concentration of this metal was lower in the most acidified scenarios when compared to control pH, indicating probable zinc mobilization from the sediment to the seawater.

1. Introduction

Global greenhouse gases (GHGs) are found in nature as a result of natural and anthropogenic processes. Carbon dioxide (CO₂) is a well-known GHG that is generated naturally in volcanoes, hot springs, groundwater, and glaciers. Volcano-based hydrothermal systems are the source of sizeable CO₂ emissions, either due to hydrothermal steam vents (Chiodini et al., 1998) or the diffuse release by degassing soils (Rogie et al., 2001; Werner et al., 2008). In magmatic hydrothermal systems, water exchanges heat with magmatic bodies at deep depths, and rises to the surface through permeable rock formations as a high-temperature plume and steam gas (mostly CO₂) (Dempsey et al., 2012). The CO₂:steam (CO₂:H₂O) mass ratio of the rising plume is known from fumarole measurements (Harvey and Harvey, 2015). This natural process results in geochemical changes in the marine environment such as the acidification of sediment and overlying water. Regarding the anthropogenic processes, since pre-industrial times, increasing emissions of GHGs due to human activities have led to a marked increase in

atmospheric concentrations of the long-lived GHGs (Barker et al., 2007). The Intergovernmental Panel on Climate Change (IPCC, 2014) attributed the increase of anthropogenic CO₂ to the high level of fossil fuel emissions (including cement production). In this sense, the U.S. National Oceanic and Atmospheric Administration (NOAA, 2017) estimated a CO₂ of 489 ppm in 2016, with an increase of 2.2 ppm per year during the last decade (2007–2016). For this reason, there is a recognition for the need to adopt measures to reduce CO₂ emissions.

Carbon capture and storage (CCS) is considered an option in the portfolio of mitigation measures for the stabilization of CO₂ concentration in the atmosphere (IPCC, 2005). This technology consists of the separation of CO₂ from industrial and energy-related sources, transport, and injection into long-term storage sites (Kirchsteiger, 2008). Potential storage sites include sub-seabed geological formations such as depleted oil and gas reservoirs and deep saline aquifers (Goldberg et al., 2008). One of the main possible environmental risks associated with this activity is the accidental CO₂ leakage from the storage sites (Bellerby and Golmen, 2013). A small, but continuous CO₂

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leakage to overlying sediment and seawater would be sufficient to cause major chemical changes, for example, the acidification of the ecosystem (Ardelan et al., 2009). Furthermore, decreases in pH could affect dissolution and desorption of metal(loid)s from sediment, resulting in their mobilization to the water column (De Orte et al., 2014).

Sediments act as a sink and a source of anthropogenic chemicals to the water column (DelValls et al., 1998). The geochemical cycle of contaminants in the marine environment is significantly determined by their interactions with sediments (Morillo et al., 2004). For this reason, sediments have been used to diagnose the quality of aquatic systems (DelValls et al., 1998). Without anthropogenic influences, the presence of metals in sediments is dominated by silicate and primary minerals, while metals introduced by human activities are associated with other phases of the sediment, such as carbonates, oxides, hydroxides, and sulfides (Heltai et al., 2005). The chemical form in which metals are present in sediments will determine its mobilization capacity and bioavailability (Morillo et al., 2004) and, consequently, its potential toxic effects to the biota. However, changes in environmental conditions, such as acidification or alteration in redox potential, might increase mobilization of metal(loid)s from solid to liquid phase.

One of the most widely used methods for determining the forms of metals in sediments is based on sequential extraction procedures (Morillo et al., 2004). A sequential solution of sediments is created using several reagents with different acidification scales in order to extract the components so that the elemental distributions in each phase of sediments can be defined. One of the first sequential chemical extraction methods was developed by Tessier et al. (1979), which formed the basis for the subsequent development of other speciation schemes. In order to standardize the various schemes developed afterwards, the European Community Bureau of Reference (BCR) proposed a three-step sequential extraction procedure. This method has been adopted by various authors and applied to a range of solid samples (Albores et al., 2000; Belazi et al., 1995; Bonnail et al., 2016a; López-Sánchez et al., 1993; Mester et al., 1998; Nieto et al., 2007).

The aim of this work was to assess the impacts of acidification on the speciation of metal(loid)s in marine sediments. Metal-contaminated sediments were collected and submitted for laboratory experimentation involving direct injection of CO₂, and the BCR sequential extraction procedure was applied to assess geochemical speciation of the metals.

2. Materials and methods

2.1. Study area

Sediment samples were collected in the Huelva Estuary (southwest of the Iberian Peninsula) since Huelva is one of the eleven different areas in Spain proposed as potential subterranean structures for CO₂ storage (BOE, 2008). The estuary is located in the confluence of the Tinto and Odiel Rivers (Fig. 1). These rivers drain the central and eastern part of the Iberian Pyrite Belt (IPB), a region long known for its intensive mining activities. Even though the majority of mining activities have been suspended since 1992 (Sarmiento, 2007), residues of massive exploitation continue to produce acid leachates that contaminate the Tinto–Odiel basin. Acid-mine drainage transported by these rivers is the main source of metal pollution into the Huelva Estuary (Sarmiento et al., 2009), but other important sources of contamination in this area include industrial residues from chemical industry plants located in the areas close to the Ría of Huelva and urban sewage from the city of Huelva. Because of the multiple sources of contamination, the Huelva Estuary is heavily contaminated by metal (loid)s, and it is considered to be one of the most polluted aqueous environments in Western Europe (Borrego et al., 2002; Caliani et al., 1997; Bonnail et al., 2016b).

Two sediment sampling sites were chosen in the Huelva Estuary: (1) Levante (LEV) is situated within the Odiel River in the inner part of the estuary, and (2) Mazagón (MZ) is located at the mouth of the estuary

(Fig. 1). In addition, a third area was selected as a control site (reference sediment): the shallow tidal creek area of the Río San Pedro (RSP), which is located some distance to the Southeast of the Huelva Estuary in the Bay of Cádiz. Although the control site is subjected to impacts from fish farming (Ferrón et al., 2009) and recreational activities, this sediment contains low levels of metals (Blasco, 2005).

2.2. Sampling

In the Huelva Estuary (Mazagón-MZ- and Levante-LEV), surface sediments (top layer from 0 to 5 cm depth) with initial water content were collected directly using 25-L plastic bucket handled by a professional diver. The water depths at each site when sampled were 1.9 m for MZ and 4.9 m for LEV. In the Rio San Pedro Estuary (RSP), sediment was collected directly using the plastic bucket because there was no water overlying the sediment at low tide.

Sediment samples were taken to the laboratory, homogenized, and sieved through 2 mm grid to eliminate debris. Sediments were stored at 4 °C in darkness for no longer than 15 days prior to the experiments. At the same time, sediments were sub-sampled and frozen at –20 °C for physico-chemical characterization. All beakers used were thoroughly cleaned with acid (10% HNO₃) and rinsed in double-deionized (Milli-Q) water prior to sampling and storage. The seawater used in the experiments was also collected from the Río San Pedro Estuary; its natural pH was 8.0 and its salinity was 30 ± 1.

2.3. Experimental set-up

The laboratory-scale CO₂ injection system (De Orte et al., 2014; Basallote et al., 2015) was adapted to 30 L test chambers with a mixture (1:4 v/v) of sediment-filtered seawater and a range of pH treatments. The automatic computed system “AT Control System” from Aqua Medic GmbH (Bissendorf) was used to control pH-electrodes (NBS scale) that were connected to the water layer in each individual aquarium. The pH was regulated by solenoid valves that delivered the CO₂ gas into each vessel. When the pH increased 0.01 U above the predetermined values, CO₂ gas bubbles were injected into each chamber—from a hose with pinholes that was placed as a spiral below the sediment section—until the required pH value was reached. More detailed information on this system can be found in De Orte et al. (2014).

2.4. CO₂-leakage experiments

The pH ranges of the experiment were established between controls (no added CO₂) and the minimum water pH reached (the values varied between sampling points). The experiment lasted 10 days and at the end of the experiment, sediment aliquots were sampled from the aquaria, stored in closed plastic bags, and immediately frozen at –20 °C until analysis.

2.5. Analytical procedure

2.5.1. Sediment characterization

Grain-size distribution was determined following the UNE 103101: 1995 (1995). The organic carbon content was measured in freeze-dried sediment according to Gaudette et al. (1974), and modified by El-Rayis (1985). In summary, it consists in a titration method using K₂Cr₂O₇, concentrated H₂SO₄, and an external heat source for the oxidation of organic carbon by means of an automatic titration device (Metrohm 888 Tritando). The percentage of organic matter was estimated by loss of ignition at 550 °C and by gravimetric determination. The mineralogical analyses were determined by X-ray diffraction (BRUKER diffractometer model D8ADVANCE) at the Central Services of Science and Technology of the University of Cádiz.

A portion of sediment was pseudo-total digested according to the International organization for Standardization procedure 11466 (ISO,

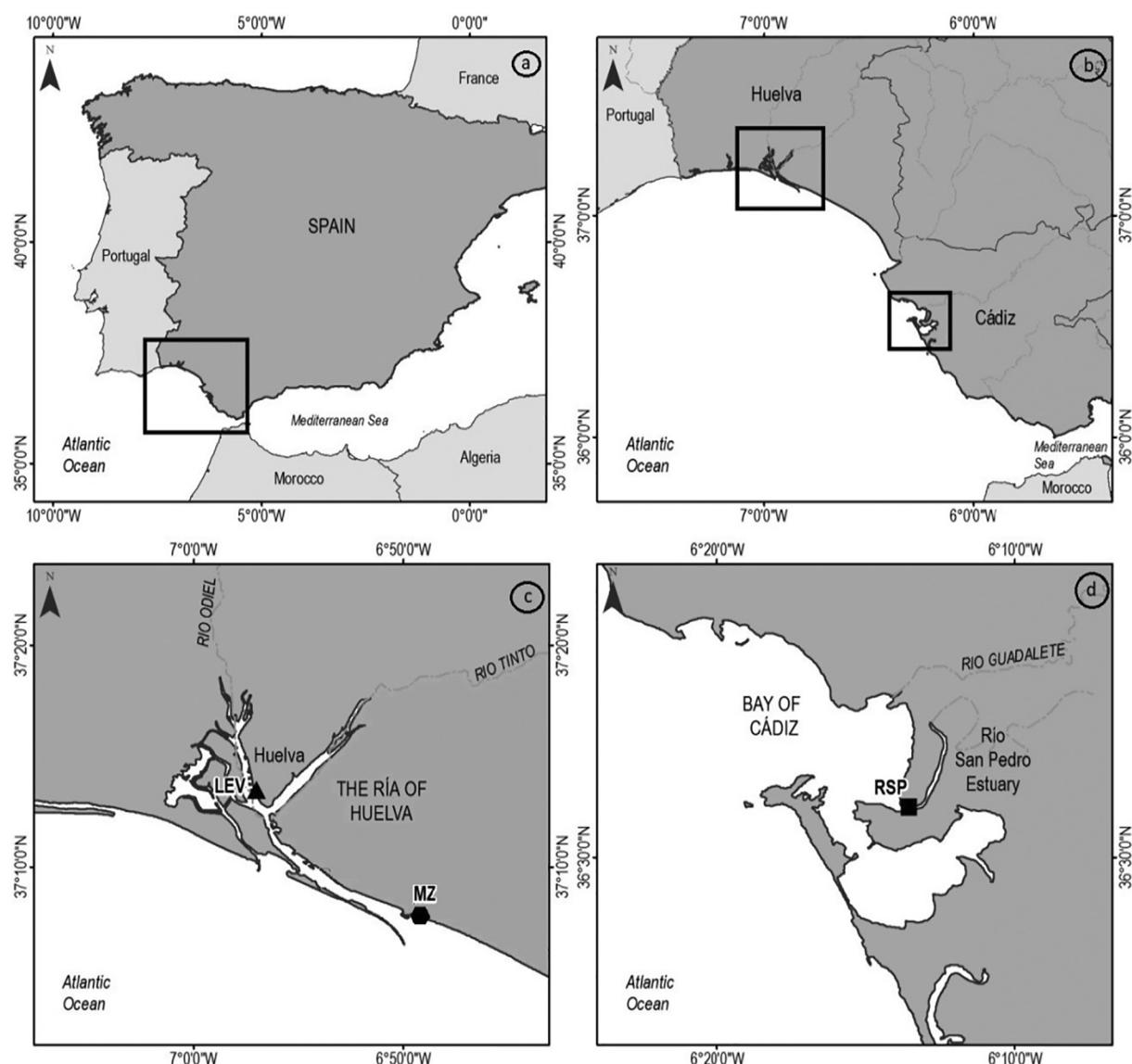


Fig. 1. Map of the two study areas located in the Southwestern (b) of the Iberian Peninsula (a), showing Huelva Estuary (c) with the sampling stations Mazagón (MZ) and Levante (LEV), and the Bay of Cádiz (d), with the sampling station Río de San Pedro (RSP).

Table 1

Reagent and method used at each extraction step of the sequential extraction procedure.

Extraction stage	Extraction reagent and method	Fraction	Extracted components
Stage 1	0.11 mol/L Acetic acid, 16 h agitation at room temperature	F1, acid soluble	Metals that are exchanged or associated with carbonates
Stage 2	0.5 mol/L hydroxyl ammonium chloride (pH 1.5), 16 h agitation at room temperature	F2, reducible	Metals associated with oxides of Fe and Mn
Stage 3	8.8 mol/L H ₂ O ₂ solution (pH 2–3), 2 h at 85 °C followed by 1.0 mol/L solution of ammonium acetate (pH 2), 16 h room temperature	F3, oxidizable	Metals associated with organic matter and sulfides
Stage 4	Mix acid HCl:HNO ₃ (3:1) 16 h room temperature followed by 2 h 130 °C	F4, residual	Metals strongly associated with the crystalline structure of minerals

1995). The metal fractionation sequence was based on the BCR method of three-step sequential extraction (Rauret et al., 1999). A forth step with aqua regia was added as a homologue of the pseudo-total digestion (Bonnai et al., 2016a). The extraction reagents used and the sediment fractions targeted are illustrated in Table 1.

2.5.2. Trace metal analysis

The trace metal(lloid) analysis (that is, the dissolved concentrations of arsenic [As], cobalt [Co], chromium [Cr], copper [Cu], iron [Fe],

nickel [Ni], lead [Pb], and zinc [Zn]) of the sediment samples was performed with an inductively coupled plasma atomic emission spectrometry (ICP-AES) (IRIS INTREPID-Thermo Elemental). This analysis was performed by the Spectroscopy Division (ICP/AAS) of the Central Services of Science and Technology of the University of Cádiz. The MESS-3 Marine Sediment Reference Material for trace metals and other constituents from the National Research Council of Canada was used to validate analytical measurements.

Table 2

Sediment characterization results (in %) for each sediment sample.

Sample	Sand	Fines	OC	OM
RSP	56.12	43.89	0.54	7.09
MZ	45.41	54.59	1.17	8.20
LEV	47.30	52.70	1.91	9.42

OC: organic carbon; OM: organic matter.

2.5.3. Statistical analysis

The effects of the different pH treatments on the behavior of metals were studied using the analysis of variance (ANOVA) followed by a Bonferroni test. Prior to this analysis, normal distribution (Shapiro-Wilk test) and homogeneity of variances (Levene's test) were checked. The software SPSS 15.0 was used for the development of statistical analyses.

3. Results and discussion

3.1. Reproducibility

The analytical procedure was checked using the reference material (MESS-3) with a percentage of recovery of approximately 100% for some elements (As and Pb) and > 80% for others (Co, Zn, and Cu).

3.2. Sediment characterization

General characteristics (granulometry, organic carbon, and organic matter content) of the sediments are presented in Table 2. Table 3 includes Eh and pH values measured in sediments according to each pH treatment. Concerning the characteristics of sediments, the values of total organic carbon, organic matter content, and proportion of fines were higher in sediments from Huelva Estuary than from the Rio San Pedro Estuary (Table 2).

The ranges of pH values of the water from the chambers (Table 3) were similar for sampling sites RSP and MZ, whereas the values differed for samples from the LEV site. The standard deviation for the pH treatments (± 0.1) refers to the variation between the replicates of the same pH, as well as the deviation occurred in one chamber during the entire experimental time (10 days). Because the variance never exceeded 0.1, this value was established for all samples.

The acidification of sediments was promoted by the injection of CO_2 for each treatment and for all of the sediment samples (Table 3). Nevertheless, decreases in pH occurred to a lesser extent when compared to seawater. The lowest pH value recorded was 6.6 in sediments from the LEV site. The pH from sediments of the MZ site varied less than those from the other sites, and the lowest value reached was 7.27. A small increase in the measured Eh values was observed with a decrease in the pH in the samples from the contaminated sites, MZ and LEV

Table 3Eh and pH values measured in sediment according to each pH treatment in the seawater after 10 days of exposure to CO_2 injection.

Site	pH treatment (value ± 0.1)	pH sediment	Eh (H) sediment
RSP	7.8	7.23	81
	7.0	7.05	128
	6.5	7.0	90
	6.0	6.7	75
MZ	7.8	7.52	0.4
	7.0	7.55	28
	6.5	7.42	16
	6.0	7.27	54
LEV	7.8	7.27	78
	7.0	7.20	74
	6.5	7.20	80
	6.0	7.15	88
	5.5	6.6	100

Table 4

Mineralogical composition (in percentage) of sediments.

Mineralogy (%)	RSP	MZ	LEV
Quartz	59.0	38.5	34.6
Calcite	21.5	2.8	
Muscovite	9.7	26.7	44.9
Phlogopite	3.3		
Montmorillonite	4.1		
Kaolinite	2.5		
Albite		32	
Hotsonite			14
Clinochlore			6.5

(Table 3).

Mineralogical analysis of the sediments (Table 4) indicates that both RSP and MZ sediments contain carbonate minerals, while LEV sediment does not. This implies a higher pH buffering capacity for MZ and RSP sediments, which can mitigate the effects of pH reductions caused by CO_2 leakages. The absence of calcite in LEV sediments could be the reason for the lower pH values observed in this site.

3.3. Metal distribution in sediments

The concentration of metal(lloid)s in marine sediment samples for each extracted fraction is illustrated in Fig. 2. The sampling point from LEV presented the highest concentration of all of the metal(lloid)s, followed by MZ. The high metal(lloid) concentrations in LEV site comes from the natural presence of these elements in the area and their discharge to Odiel-Tinto River as a result of long-term mining activities (Bonnail et al., 2016a). Metal(loid) precipitation processes to the sediment takes place as the Rivers approach seawater due to the changes in the pH and salinity. In general, the concentration levels for metal(lloid)s measured in this work were similar to those reported by Morillo et al. (2004) in Huelva Estuary (considering areas near our sampling point MZ), especially with regard to the metals Zn, Pb, Ni, and Cr. Arsenic concentrations in RSP site were under the detection limits of the equipment and therefore this site was not included in Fig. 2.

The percentage of elements extracted in each fraction is shown in Fig. 3. This percentage was calculated from the ratio between the concentration of the element in each fraction, and the sum of the concentrations in all fractions. Metals had similar distribution patterns in the sediment samples from the Huelva Estuary; whereas in the RSP, the distribution patterns differed. The mobile fractions (F1 and F2) of the most studied elements were null in sediments from the RSP.

The metal(lloid)s As, Cr, Fe, and Ni displayed similar behaviors. They presented higher proportions of the residual fraction (F4), accounting for > 55% of their total concentration in all the studied sites (except for As, which was only detected in Huelva Estuary). These results align with previously reported data, especially for Cr and Ni (Martín et al., 1998; Sekhar et al., 2003; Yuan et al., 2004). Our results also agree with previously reported data from Huelva Estuary, in which Cr and Ni were predominant in the residual fraction (Bonnail et al., 2016a; Morillo et al., 2004). Metals in the F4 fraction are not likely to be released into the water column because they are trapped within the crystal structure of the minerals, so they remain unavailable to the aquatic system. Regarding Fe, it is one of the most common elements in the Earth's crust, and great proportions of this metal were expected to be present in the residual phase (Morillo et al., 2004), as observed in the present work and reported elsewhere (Yuan et al., 2004).

Among the metals analyzed, Cu presented the highest proportion in the oxidizable fraction (F3). Large amounts of Cu have previously been observed in this fraction (Li et al., 2007; Morillo et al., 2004; Passos et al., 2010); this observation is probably due to the high affinity of this metal to humic substances, which makes up the large portion of natural organic matter in sediment. The metals present in this phase can

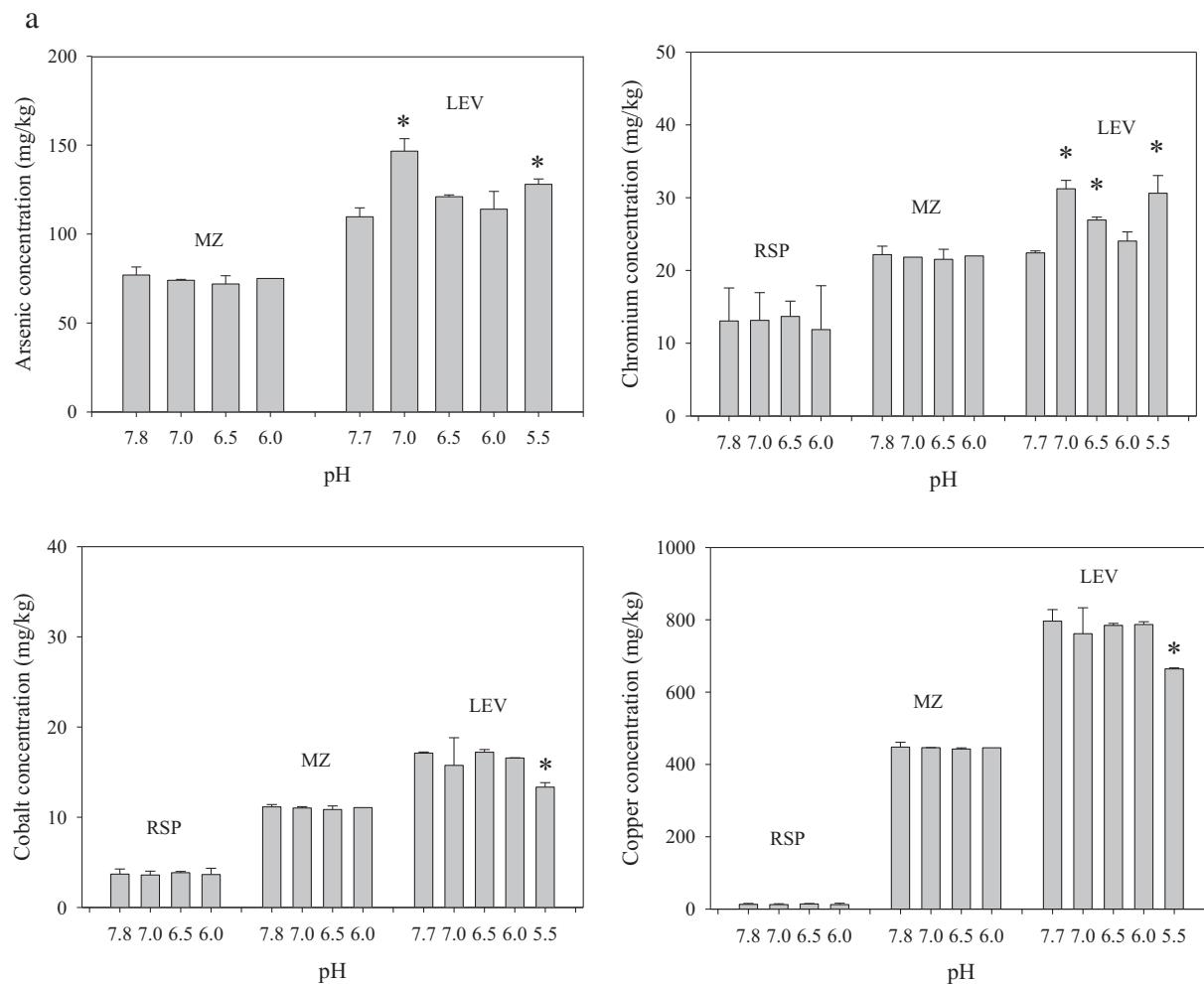


Fig. 2. Concentration of the metals As, Co, Cr, Cu, Fe, Ni, Pb and Zn for the sediments from Río de San Pedro Estuary (RSP), Mazagón (MZ) and Levante (LEV) exposed to different pH treatment (Control, 7.0, 6.5, 6.0, and 5.5). The symbols (*) refers to significant differences ($p < 0.05$) with the control pH.

become bioavailable if degradation of organic matter or oxidation of sulfides occurs, releasing the metal into the water column.

With respect to the reducible phase (F2), Pb represented > 50% of the total sample concentration at the sites from the Huelva Estuary. This result suggests that Fe and Mn are important carriers for Pb in sediments; this behavior was also observed by other authors (Mahanta and Bhattacharyya, 2011; Morillo et al., 2004; Passos et al., 2010). It is important to mention that Pb is highly particle reactive and can coprecipitate with Fe–Mn oxyhydroxides or can be adsorbed on the surface of metal oxyhydroxide. Therefore, changes in the oxidation state of Fe and Mn can release Pb and other metals into the water column, becoming a source of contamination (Wasay et al., 2001). In RSP, total concentration of Pb was low, and the main proportion was measured in the oxidizable fraction (F3).

Metals in the F1 fraction represent a great environmental risk because they are weakly bound to sediments and, therefore, more available to the aquatic system. Within the metals measured in this work, Zn was found in the greatest proportion in this fraction; however, this was only observed in the sites from the Huelva Estuary. As previously mentioned, the Huelva Estuary is affected by several sources of contamination, with a high concentration of toxic metals. A high percentage of Zn in the most labile sediment fraction has also been found in other studies performed in polluted areas (Passos et al., 2010; Sekhar et al., 2003), including Huelva Estuary (Morillo et al., 2004). In the RSP site, where metal contamination is considered low, the proportion of Zn in the most mobile fraction was low (F1 = 5%), and the highest

percentage of this metal (41%) was detected in the residual phase.

In spite of the low concentration of the metal Co in all the studied stations, the concentration was homogeneously distributed among the four fractions from the Huelva Estuary. At RSP this metal was mainly measured in the F3 and F4 fractions (86%).

3.4. Risk characterization

To evaluate the biological risk of sediment-bound contaminants without biological effects data, international organizations provide the sediment quality guidelines (SQGs). These concentrations are estimates of a probable effect, and are based on the total concentration of metal in the environment. While these values are considered to be references for previous screening risk assessments; international environmental agencies recommend the development of guidelines that are adequate to each region in terms of the geological composition and local biology. From Table 5 it is possible to contrast the total metal concentration of elements in the sediments of this study and the thresholds established by international (NOAA and the U.S. Environmental Protection Agency [USEPA]) and national (CEDEX) regulatory bodies.

According to any of the guidelines presented in Table 5, all of the elements analyzed in RSP sediments are below the reference values—that is, this site is considered to be non-contaminated and do not pose a risk for biota. In contrast, the LEV and MZ sediments register important risk concentrations of As, Cu, Pb, and Zn, which surpass the probable effect level (PEL) of the NOAA and the USEPA. In Spain, the

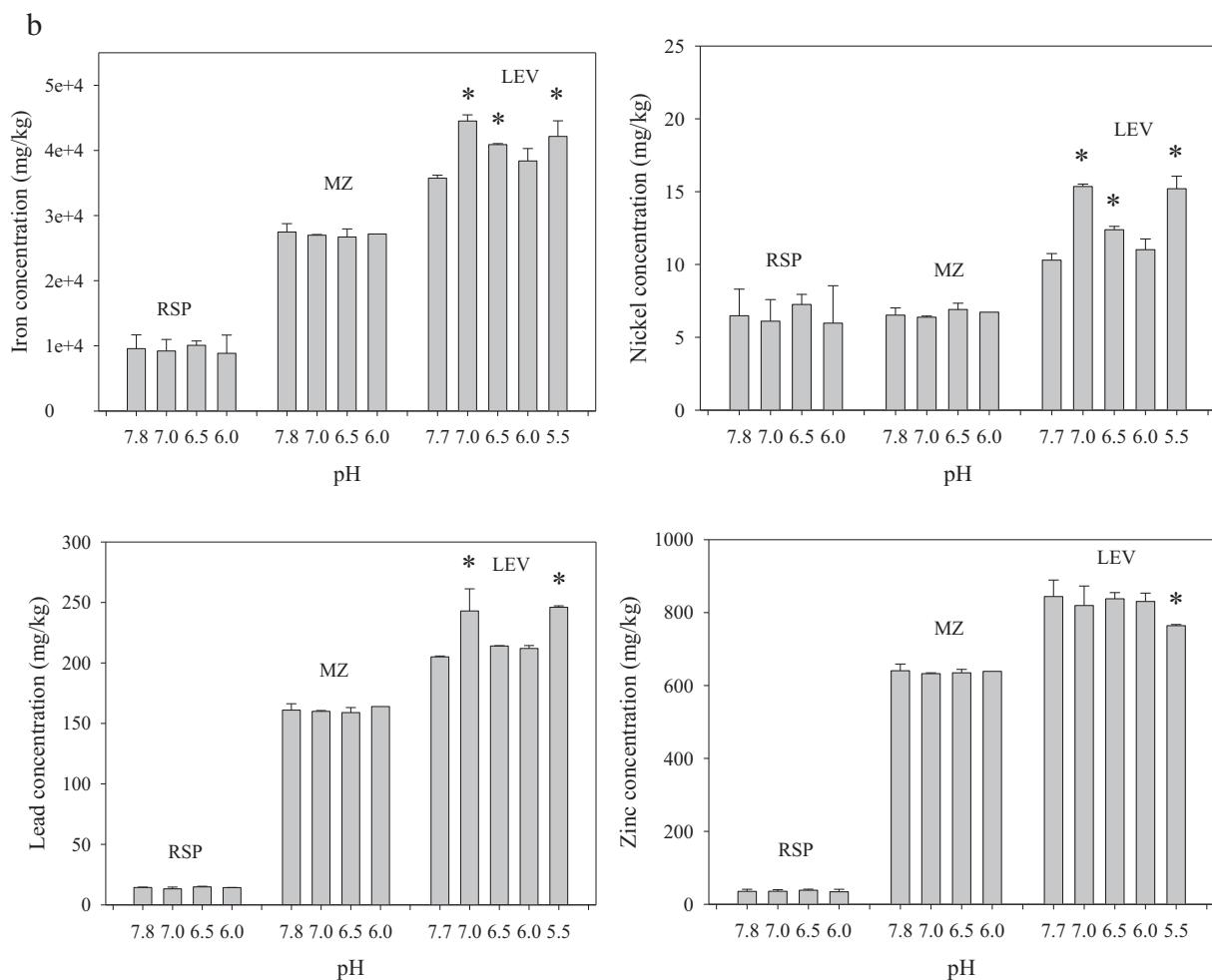


Fig. 2. (continued)

SQG (or action levels [AL]) are recommendations adapted from dredge material studies for Spanish ports (including Huelva), and are carried out by CEDEX. Attending the baseline of AL1, the estuarine area of Huelva required actuation for As, Cu, Pb, and Zn.

In addition to SQGs, assessing the distribution of metals and metalloids within the different fractions of sediments is useful to indicate their availability and the potential risk to aquatic ecosystems. Here, sediments were classified according to a *Risk Assessment Code* (RAC) (Fig. 4). The RAC has been previously used in studies of metal pollution in sediments (see, for example, Delgado et al., 2011). This method considers the percentage of metals in the F1 fraction of sediments—that is, the exchangeable and carbonate fractions. When the percentage of metal is lower than 1%, there is no risk; between 1%–10%, the risk is low; between 11%–30%, the risk is medium; between 31%–50%, this risk is high; and > 50%, the risk is considered to be very high. According to this evaluation, results showed that in sediment from RSP, Co (F1 = 14%) represented a medium risk, Zn (F1 = 5%) was a low risk, and the other metals did not represent any risk (F1 < 0%). For the sediments from the Huelva Estuary, Zn was considered to be high risk (39% and 43% for MZ and LEV, respectively), and Co was medium risk (28% and 23% for MZ and LEV, respectively).

3.5. Variation of metal distribution pattern with pH

For RSP and MZ no significant changes in metal concentration according to pH was observed. For LEV site, increases in the concentration of some metals were observed following CO₂ injection (As, Cr, Fe, Ni and Pb) while for other metals, total amounts decreased (Co, Cu and

Zn). Those increases indicate precipitation processes. In this sense, the removal of metals from the water column can be caused by adsorption to Fe precipitates (Bonnail et al., 2016a). Removal of As from the seawater at lower pH treatments was previously observed (De Orte et al., 2014; Asta et al., 2009) and can be explained by the high affinity of As to iron oxides. In Fact, Fe (III)-precipitates is the main mechanism responsible for arsenic migration in an oxidizing environment (Sarmiento et al., 2009). Iron precipitates could also be influencing the removal of the other metals. On the other hand, decreases of metal amounts might indicate mobilization to the water column. At the LEV site, total concentrations of Cu decreased from 796 mg/kg at the control pH (no CO₂ injection) to 694 mg/kg at the minimum pH tested (pH 5.5.); in contrast, Cu concentrations in sediments from the MZ site decreased from 457 mg/kg (control) to 446 (pH 6.0). Zinc concentrations measured in the sediments also varied among different pH scenarios. Concentrations of Zn decreased from 844 for the control to 764 mg/kg for the minimum pH tested in samples from the LEV site, and from 653 for the control to 639 mg/kg for the minimum pH tested in samples from the MZ site.

The amount of Cu and Zn in each one of the four fractions on the basis of pH treatments from samples obtained from the LEV and MZ sites are shown in Fig. 5. Reductions in the concentration of Cu were more intense in the oxidizable fraction, which also accounted for the highest proportion of this metal between the four fractions. This phase is related to the metals that are associated with organic matter and sulfides. This result might be attributed to the fact that sediments from the Huelva Estuary contain a large reservoir of neofomed sulfides (Fernández-Caliani et al., 1997; Monterde, 2004; Schippers and Jorgensen, 2002). Small increases in Eh values can result in oxidation

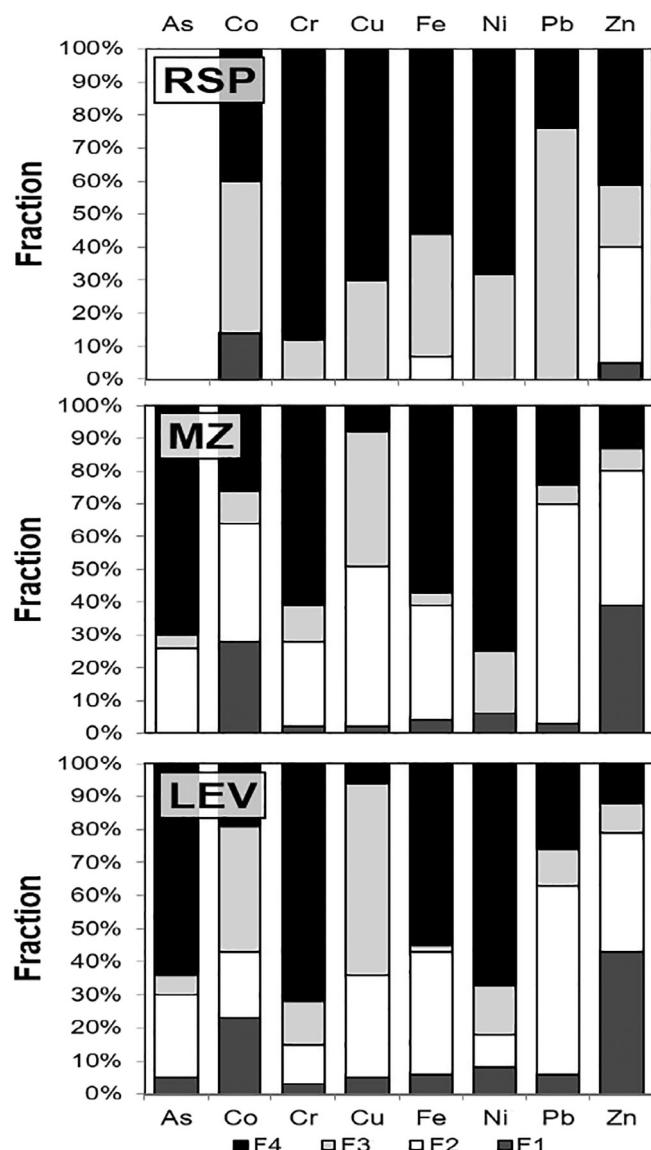


Fig. 3. Metal(lloid)s concentration distribution in the different chemical fractions of sediments as percentages.

processes, causing the release of metals associated with sulfides from the sediment. As already mentioned, decreases in pH values resulted in increases in Eh values in sediments from Huelva Estuary; this finding appears to play a role in the process leading to decreases in the total amount of Cu in the sediment samples and leading to the release of this

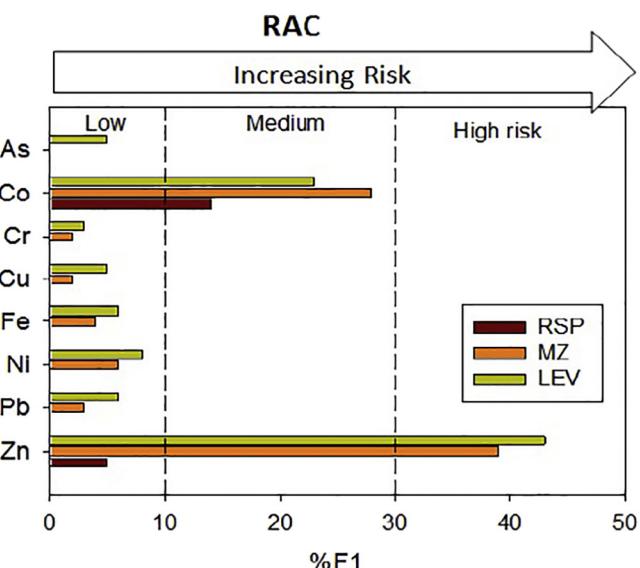


Fig. 4. Classification of the elements based on its exchangeable fraction in accordance to the Risk Assessment Code (RAC) for the different stations.

metal into the water column.

With regard to Zn, reductions in its total concentration at the lowest pH treatment took place primarily in F1 (Fig. 5). As stated, this fraction accounts for metal(lloid)s that are exchangeable or associated with carbonates. Here, metals are weakly attached to sediments and are therefore vulnerable to any changes in environmental conditions. CO₂-related acidification enhances the potential of this metal to leach into the water and spread through the environment. Measured concentrations of both Cu and Zn were high, especially in samples from the LEV site. This is a serious concern because both metals are toxic to marine organisms. In fact, concentrations of both metals were found in tissues of the lugworm *Arenicola marina* in experiments with sediments from Huelva Estuary (Kalman, 2009), and they were also related to histopathological damage and toxicity to several organisms (Riba, 2003).

Decreases in Cu and Zn concentrations were more intense in samples from the LEV site compared to the MZ (see Fig. 5). In the latter site, the pH of the sediment had smaller variations than sediments from the LEV site (Table 3). Furthermore, aquariums containing LEV sediment achieved the lowest water pH value (pH 5.5) within the three sediments tested.

4. Conclusions

Acidification processes may produce chemical changes in the sediment–water interface, leading to several geochemical alterations that could influence the behavior of metals between sediment and the water

Table 5

	As	Cr	Cu	Ni	Pb	Zn
RSP	bdl	13.2	13.3	5.84	12.5	32.5
MZ	83.7	21.4	448	8.85	155	611
LEV	161	30.3	800	17.0	203	814
CEDEX ^a	A	B	A	B	A	A
	80	200	200	400	100	400
NOAA ^b	7.24	41.6	52.3	108.2	15.9	42.8
USEPA ^c	8.2	70	81	270	20.9	51.6
					46.7	218
						150
						410

bdl: below detection limits.

^a SQVs proposed by the Centro de Estudios y Experimentación de Obras Públicas (CEDEX, 1994) of Spain. A: action level 1- AL₁; B: action level 2- AL₂.

^b Marine SQGs of the National Oceanic and Atmospheric Association (NOAA, 2007). Adopted from Buchman (1999).

^c Marine and estuarine SQGs of the U.S. Environmental Protection Agency (USEPA). Adopted from Long et al. (1995). A: TEL- Threshold Effect Level; B: PEL- Probable Effect Level.

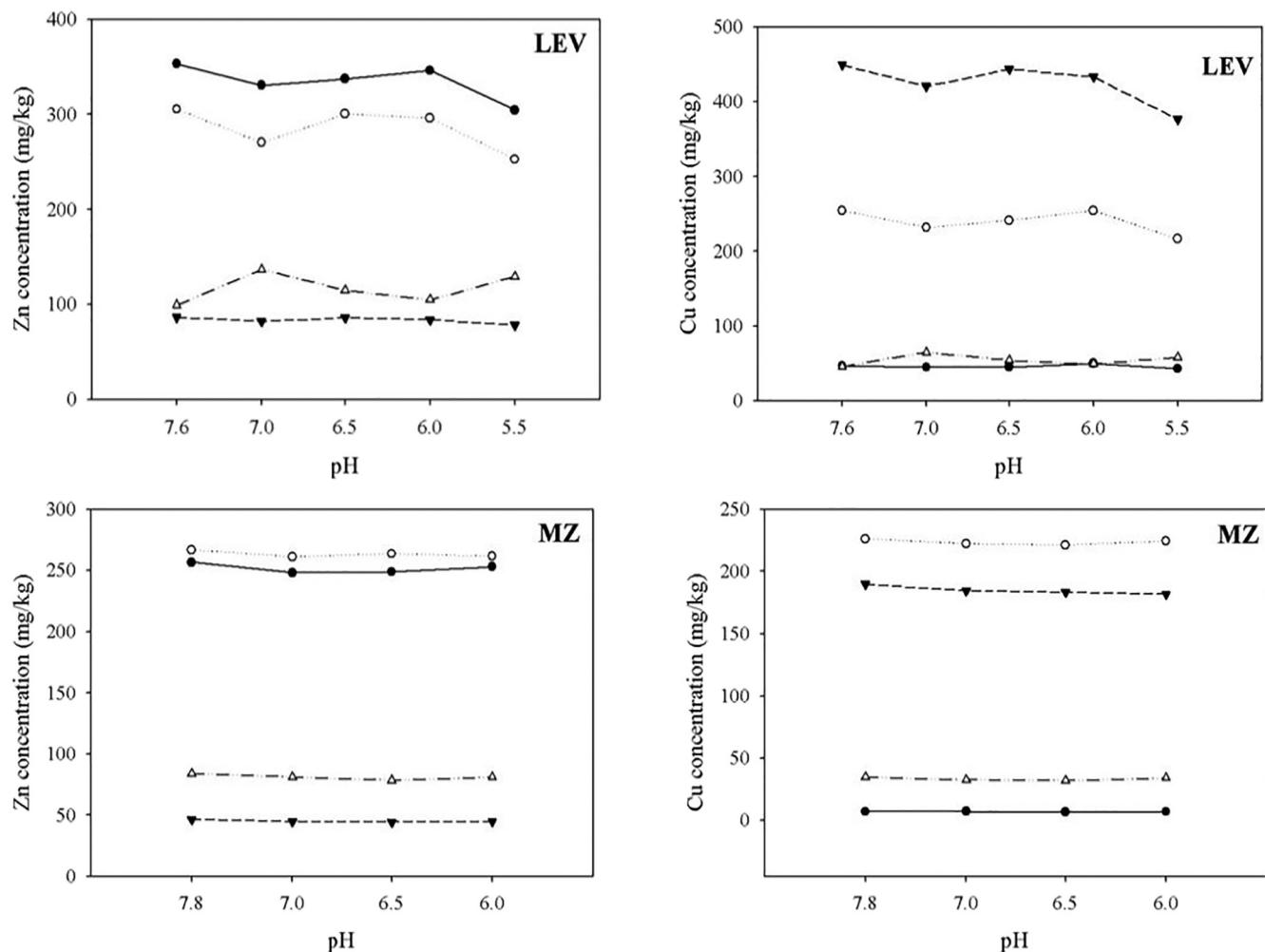


Fig. 5. Zn and Cu concentration (mg/kg dw) at each sediment fraction according to pH. - ●:F1, ○:F2, ▼:F3, △:F4.

column. The behavior of metal(loid)s in sediments depends on their association with the different phases, and this is a key factor for the determination of the mobility and bioavailability of the metals. Sequential extraction procedures applied in this work showed that the metal with the highest proportion in the most mobile fraction of the sediments was Zn. In this sense, calculated risk assessment code indicate that this metal represents high environmental risk in both sites from the Huelva Estuary. Furthermore, the concentration of this metal was lower in the most acidified samples suggesting that pH decreases resulted in Zn mobilization from the sediments of the Huelva Estuary into the water column. Decreases in pH also resulted in changes in the redox potential of sediments, which probably caused the oxidation of neoformed sulfides and, consequently, Cu mobilization, considering that Cu was mostly retained in the fraction of sediment associated with sulfides and organic matter. In samples from the MZ site, pH values varied less than other sediments, probably due to a higher buffering capacity, which could be the reason for a less intense metal mobilization when compared to the LEV site.

In this work we observed that the specific processes leading to the mobilization of the hazardous constituents from sediments and the magnitude of their effects will depend on site-specific conditions, including the properties of the sediments, such as granulometry, mineralogy, and the degree of metal(loid)s contamination where the leakage occurs. The data obtained here provide insight on the consequences of carbon dioxide leakage during carbon capture and storage activities.

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